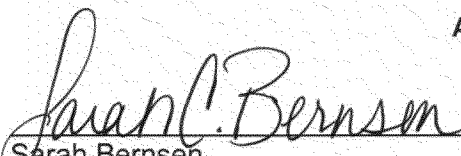
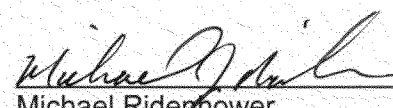
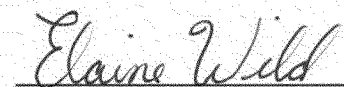
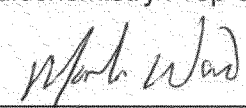
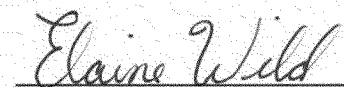


**Title: ISOTOPIC THORIUM, PLUTONIUM AND URANIUM IN VARIOUS
MATRICES BY EICHROM® SEPARATION RESINS**

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1.0 SCOPE AND APPLICATION

- 1.1 This SOP provides a rapid, reliable method for separation of Thorium, Plutonium and Uranium in various matrices.
 - 1.1.1 If only Uranium analysis is requested, see SOP: ST-RC-0238.
 - 1.1.2 If other actinides in addition to Thorium, Plutonium and Uranium are requested, please see SOP index to determine applicable SOP.
- 1.2 This SOP is based on Eichrom Technologies, Inc. Analytical Procedures “ACW13 VBS Thorium, Plutonium and Uranium in Water (with Vacuum Box System)” and “ACW01 Uranium and Thorium in Water”.
- 1.3 This procedure is applicable to water, soil, filter, biota, and oil.
 - 1.3.1 Soil, filter, biota and oils are pre-prepared in accordance with SOP, ST-RC-0004.
 - 1.3.2 Water preparation is contained within this SOP.
- 1.4 The requested limits, minimum detection amounts and QC limits are maintained in the Laboratory Information Management System (LIMS).

2.0 SUMMARY OF METHOD

- 2.1 This SOP describes the method for separation of Thorium, Plutonium and Uranium using Eichrom resin prior to measurement by alpha spectrometry. A calcium phosphate precipitation technique is used to concentrate and remove actinides from water samples. Soils, Sludge and Filters are prepared for analysis using ST-RC-0004. Tracers are used to correct for chemical recovery and correct results to improve precision and accuracy.

3.0 DEFINITIONS

- 3.1 See the TestAmerica Quality Assurance Manual (ST-QAM) for a glossary of common terms and data qualifiers.
- 3.2 Tracer - A known amount of ²³²Uranium, ²²⁹Thorium, ²⁴²Plutonium, (or ²³⁶Plutonium), added to each sample to determine chemical yield. The tracer serves as an internal standard, which is used to calculate the activity of the target isotopes.

4.0 INTERFERENCES

- 4.1 Actinides with unresolvable alpha energies, such as Americium-241 and Plutonium-238, must be chemically separated to enable measurement of the target actinide(s). This method separates these isotopes effectively.
- 4.2 Samples that are high in carbonates and phosphates, as indicated by a violent and vigorous reaction during the initial phases of digestion, need to be loaded in a minimum of 40 mL of load solution. The increased amount of load increases the amount of aluminum nitrate that the samples are exposed to. The extra aluminum nitrate helps to bind phosphates which interfere with thorium uptake.
- 4.3 Neptunium-237 can interfere with the Plutonium-242. This interference can be avoided by increasing the normality of the hydrochloric acid rinse and increasing the concentration of the titanium trichloride eluant.

5.0 SAFETY

- 5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of

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the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

5.1.1 None.

5.2 PRIMARY MATERIALS USED

5.2.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material ⁽¹⁾	Hazards	Exposure Limit ⁽²⁾	Signs and symptoms of exposure
Ammonium Hydroxide	Poison Corrosive	50 ppm (TWA)	Inhalation symptoms include irritation to the respiratory tract. Ingestion symptoms include pain in the mouth, chest, and abdomen, with coughing, vomiting and collapse. Skin contact causes irritation and burns. Eye contact with vapors causes irritation.
Calcium nitrate	Oxidizer	None established	Inhalation symptoms include coughing and shortness of breath. Skin contact symptoms include redness, itching, and pain. Eye contact causes irritation, redness and pain.
Hydrochloric Acid	Poison Corrosive	5 ppm (Ceiling)	Inhalation symptoms include coughing, choking, inflammation of the nose, throat, and upper respiratory tract. Skin contact can cause redness, pain, severe skin burns, and discoloration. Vapors are irritating to the eyes. Contact may cause severe burns.
Hydrofluoric Acid	Poison Corrosive	3 ppm (TWA)	Inhalation symptoms may include sore throat, coughing, labored breathing and lung congestion/inflammation. Skin contact may cause serious burns which are not immediately apparent or painful. Symptoms of eye contact include redness, pain, and blurred vision.
Lead nitrate	Poison Oxidizer	0.05 mg/m ³ (TWA)	Inhalation of lead can produce local irritation of bronchia and lungs with acute exposure causing a metallic taste in the mouth and chest and abdominal pain. Ingestion symptoms can include abdominal pain and spasms, nausea, vomiting, and headache. Absorption through skin can occur causing symptoms similar to ingestion. Skin contact may cause local irritation, redness and pain. Absorption can also occur through eye tissue.
Nitric Acid	Corrosive Poison Oxidizer	2 ppm (TWA) 4 ppm (STEL)	Inhalation may cause coughing, choking, and irritation of the nose, throat, and respiratory tract. Skin contact can cause redness, pain, and severe skin burns. Concentrated solutions can stain the skin a yellow-brown color. Vapors are irritating to the eyes and contact may cause severe burns.
Sulfuric Acid	Corrosive Poison Cancer Hazard	1 mg/m ³ (TWA)	Inhalation may cause irritation of the nose and throat, and labored breathing. Skin contact symptoms include redness, pain, and severe burning. Eye contact can cause blurred vision, redness, pain, and severe tissue burns.

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1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.
TWA – Time Weighted Average
STEL – Short term exposure limit
Ceiling – At no time should this exposure limit be exceeded.

6.0 EQUIPMENT AND SUPPLIES

- 6.1 Beakers, 150-2000 mL
- 6.2 Analytical balance - 0.0001 g sensitivity
- 6.3 Centrifuge
- 6.4 Centrifuge tubes, poly, 50 mL with cap
- 6.5 Pipettes, glass or plastic, disposable
- 6.6 Pipettes, mechanical
- 6.7 Fume hood
- 6.8 Hotplate
- 6.9 Vortex mixer
- 6.10 pH strips, narrow range
- 6.11 Vacuum Box, Eichrom part number AC-24-BOX, or equivalent
- 6.12 Syringe filter, 25 mm acrodisc, 0.45 or 0.70 μ m
- 6.13 Cartridge reservoirs/syringe/funnel-20 mL B-D Luer Lok syringe Part Number 301625 (Fisher part number 14-823-2B), or equivalent.

7.0 REAGENTS AND STANDARDS

- 7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.
- 7.2 DI Water, obtained from the Milli-Q unit.
- 7.3 Aluminum Nitrate, solid.
- 7.4 Ammonium hydrogen phosphate dibasic (3.2M)
 - 7.4.1 Dissolve 104 g of $(\text{NH}_4)_2\text{HPO}_4$ in 200 mL of water, heat gently to dissolve, and dilute to 250 mL with water.
- 7.5 Ammonium hydroxide (NH_4OH), Reagent.
- 7.6 Ammonium Thiocyanate, crystals
 - 7.6.1 Dissolve 7.6g of ammonium thiocyanate crystals in 90 mL of DI water. Dilute to 100 mL.
- 7.7 L (+) Ascorbic Acid, reagent powder.

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- 7.7.1 L (+) Ascorbic Acid solution, 2.5 g dissolved in 10 mL of DI water.
- 7.8 Bromocresol Purple indicator solution
 - 7.8.1 Dissolve 0.20 g of Bromocresol Purple (520.24 F.W.) in 250 mL of water, add 1 mL of concentrated Ammonium Hydroxide.
- 7.9 Calcium nitrate (1.25M)
 - 7.9.1 Dissolve 51 g of $\text{Ca}(\text{NO}_3)_2$ in 100 mL of water and dilute to 250 mL with water.
- 7.10 Hydrochloric acid (12M) - concentrated HCl (sp gr 1.19).
 - 7.10.1 Hydrochloric acid (9M) - Add 1500 mL of concentrated HCl (sp gr 1.19) to 200 mL of water and dilute to 2 liters.
 - 7.10.2 Hydrochloric acid (6M) - Add 1000 mL of concentrated HCl (sp gr 1.19) to 200 mL of water and dilute to 2 liters
 - 7.10.3 Hydrochloric acid (1M) - Add 167 mL of concentrated HCl (sp gr 1.19) to 200 mL of water and dilute to 2 liters
- 7.11 Hydrochloric acid (5M) - 0.05M oxalic acid solution
 - 7.11.1 Add 12.6 grams of oxalic acid dihydrate in approximately 800 mL of water. Add 834 mL of concentrated hydrochloric acid. Dilute to 2 liters, add a stir bar, and place on stir plate until oxalic acid is completely dissolved
- 7.12 Lead Nitrate (Reagent, crystals).
 - 7.12.1 Lead Nitrate 1 % wt/vol. solution. Dissolve 1 g of lead nitrate crystals in 100 mL of DI water.
- 7.13 Nitric acid (16M) - concentrated HNO_3 (sp gr 1.42).
 - 7.13.1 Nitric acid (3M) – Add 375 mL of concentrated nitric acid to 1500 mL of DI water and dilute to 2 L.
- 7.14 Load solution [Nitric acid (3 M) - aluminum nitrate (1 M)]
 - 7.14.1 Weigh 1500 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 4 liter beaker. Add 800 mL of water(first) and 764 mL of concentrated nitric acid. Dilute to 4 L with water. Add stir bar, cover with watch glass and place on stir plate until aluminum nitrate is dissolved.
- 7.15 Potassium Hydroxide, KOH
- 7.16 Potassium Sulfate (Reagent Crystals).
- 7.17 Oxalic Acid, reagent, crystals.
- 7.18 Sodium Nitrite, NaNO_2 reagent crystals.
 - 7.18.1 Sodium Nitrite Solution – dissolve 1.0 grams of sodium nitrite crystals in 10 mL of DI water.
- 7.19 Titanium trichloride, TiCl_3 , 10% solution, commercially available.
- 7.20 TEVA Resin - prepacked column, 100-150 micron resin, or 50-100 micron prepacked cartridges.
- 7.21 UTEVA Resin-prepacked column, 100-150 micron resin, or 50-100 micron prepacked cartridges.
- 7.22 Plutonium-242 tracer standard, 10-20 dpm/mL (Plutonium-236 can also be used).
- 7.23 Plutonium-238 and/or Plutonium-239.
- 7.24 Thorium-229, 10-20 dpm/mL.

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- 7.25 Natural Thorium spike standard (Thorium-232/Thorium-228), approximately 10-20 dpm/mL.
- 7.26 Thorium-230 spike standard, approximately 10-20 dpm/mL.
- 7.27 TRM solid reference material.
- 7.28 Uranium-232 tracer, approximately 10-20dpm/mL.
 - 7.28.1 Clean uranium free of Th-228 daughter, removed by lead sulfate precipitation, activity verified prior to use. A Th-228 free Uranium-232 standard may be made as described below.
 - 7.28.2 Dilute the appropriate aliquot of stock to about 40mL with DI water.
 - 7.28.3 Add 3 grams of potassium sulfate.
 - 7.28.4 Adjust the pH to 1.5 using narrow range pH strips with either 2M H₂SO₄ or 2M KOH.
 - 7.28.5 While mixing, slowly add 25 mL of 1% Pb(NO₃)₂.
 - 7.28.6 Adjust the pH to 1.5 using narrow range pH strips with either 2M H₂SO₄ or 2M KOH.
 - 7.28.7 Dilute to 100 mL with water, and mix well. Solution should be spun (at a rate fast enough to form a vortex) continuously for at least 30 minutes to remove any Thorium that maybe in solution.
 - 7.28.8 Let stand for at least 1 hour. Centrifuge the solution for 30 minutes. Use the clean U-232 solution as soon as possible after removing the Th-228.
 - 7.28.9 Before each use, shake the standard at least 30 minutes (to absorb any ingrown Th-228 onto the sulfate precipitate), and let the precipitate settle (centrifuge). Do not disturb the precipitate while using the standard.

8.0 SAMPLE COLLECTION, PRESERVATIVES AND STORAGE

- 8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.
- 8.2 Samples may be collected in glass or plastic containers.
- 8.3 Aqueous samples are preserved with nitric acid to a pH of less than 2.
 - 8.3.1 The pH of aqueous samples are checked upon receipt by sample control, therefore, the pH does not require checking prior to analysis.
 - 8.3.1.1 Aqueous samples acidified upon receipt (designated by label on the bottle) do require checking the pH prior to analysis.
- 8.4 Solid sample requirements are found in SOP ST-RC-0004, "Preparation of Soil, Sludge, Filter, Biota and Oil/Grease Samples for Actinide Analysis".

9.0 QUALITY CONTROL

- 9.1 **Batch**
 - 9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents. Where no preparation method exists (e.g. water sample volatile organics, water sample anion analysis) the batch comprises of a maximum of 20 environmental samples which are analyzed together with the same process, lots of reagents and personnel.
 - 9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.
 - 9.1.3 For this analysis, batch QC consists of a method blank (MB), a Laboratory Control Sample (LCS), and Sample Duplicate. In the event that there is insufficient sample to analyze a sample duplicate, an LCS Duplicate (LCSD) is prepared and analyzed.

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9.1.3.1 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) may be performed upon client request, and are noted in the Client Requirement Sheets and Log-in.

9.1.4 Samples having different QC codes, due to non-standard client specific QC requirements, must be batched separately in the LIMS. A method blank and LCS may be shared across QC codes provided the actual "sample batch" does not exceed 20 environmental samples. Duplicates (and MS/MSD if applicable) must be performed for each separate QC code.

9.2 **Method Blank (MB)**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 For Water analyses, the method blank is comprised of DI water with Nitric Acid.

9.2.4 For non-aqueous analyses, the method blank is comprised of 1.25M Calcium Nitrate. See the soil preparation SOP ST-RC-0004.

9.3 **Laboratory Control Sample (LCS)**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 An LCS must be prepared with every sample batch.

9.3.3 For Water analyses, the LCS is comprised of DI water with Nitric acid fortified with the isotopes of interest.

9.3.4 For non-aqueous analyses, the LCS is comprised of a TRM sold reference material or 1.25M Calcium Nitrate fortified with the isotopes of interest. See the soil prep SOP ST-RC-0004.

9.3.4.1 For Am, Cm, Pu, Uranium only, use Calcium nitrate

9.3.4.2 For Thorium use the TRM standard.

9.4 **Matrix Spike(MS)/Matrix Spike Duplicate(MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 MS/MSD samples do not count towards the 20 environmental samples in a sample batch.

9.4.3 MS/MSD samples, when requested, must be performed with every sample batch and every LIMS batch.

9.5 **Sample Duplicate (SD)**

9.5.1 A Sample Duplicate is an additional aliquot of a field sample taken through the entire analytical process to demonstrate precision.

9.5.2 If there is insufficient sample to perform a Sample Duplicate, a duplicate LCS is analyzed. A NCM is written to document the insufficient volume and utilizing of a LCSD for demonstration of precision.

9.6 **Procedural Variations/ Nonconformance and Corrective Action**

9.6.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.6.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Balance and pipette calibrations must be checked daily when used. Refer to SOP ST-QA-0005, "Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes."

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11.0 PROCEDURE

- 11.1 For NON-AQUEOUS matrices (soil, oil, biota, etc) see SOP: ST -RC-0004 for initial sample preparation and proceed to section 11.5 of this SOP.
- 11.2 Water Sample Preparation:
- 11.2.1 If not already pre-filtered, and the client has requested analysis on a filtered fraction, filter the sample through a 0.45 micron filter. If the sample contains a large amount of sediment which would not be possible to work with, contact the manager/supervisor.
 - 11.2.2 Prepare method blank and LCS using 500 ml or 1000 ml DI water (match to volume of associated samples).
 - 11.2.2.1 Acidify with nitric acid to a pH < 2.
 - 11.2.3 Shake the sample to suspend any residue and to ensure that the sample is homogeneous.
 - 11.2.4 Weigh approximately 500mL or 1000 mL (depending on the detection limit) of sample into an appropriate size beaker. Record weight in LIMS.
 - 11.2.4.1 Aqueous sample aliquot volumes are determined by mass and use an assumed density of 1g/mL.
 - 11.2.4.2 If upon visual inspection a sample is suspected to have a high density (>1.2g/mL, e.g. brine or waste) or a low density (<0.98g/mL, e.g. mixed solvent) the sample density will be measured and the volume determined arithmetically (sample mass divided by density equals volume).
 - 11.2.5 Add appropriate tracers or standards. Generally 10 – 20 dpm of each of the Thorium, Uranium and Plutonium tracers are added. (Typically 0.1 mL or 0.2 mL depending on the reporting limit)
 - 11.2.5.1 Spike LCS and MS (if applicable) with isotopes of interest. (Typically 0.1 mL or 0.2 mL depending on the reporting limit)
- 11.3 Evaporation (Alternative option to Calcium Phosphate precipitation):
- 11.3.1 This option may be used when large sample volumes are needed to achieve low level reporting limits.
 - 11.3.1.1 Consult Manager/Supervisor to determine when this option should be used.
 - 11.3.2 Evaporate sample on a hot plate to less than 50 mL and transfer to a 100 mL beaker.
 - 11.3.2.1 Note: For some water samples, calcium sulfate formation may occur during evaporation. If this occurs, use the calcium phosphate precipitation option in step 11.4
 - 11.3.3 Gently evaporate the sample to dryness and redissolve in approximately 5 mL of concentrated HNO₃ (sp gr 1.42). Repeat step two more times, evaporate to dryness and proceed to step 11.5.
- 11.4 Calcium phosphate precipitation:
- 11.4.1 Add 0.5 mL of 1.25M Ca(NO₃)₂ to each beaker.
 - 11.4.2 Add 0.200 mL of 3.2 M (NH₄)₂HPO₄ solution to each beaker
 - 11.4.3 Add 3-5 drops Bromocresol Purple indicator to each beaker.
 - 11.4.4 Stir using the bulb of a transfer pipette and place beaker on a hot plate.
 - 11.4.5 Allow the samples to heat to near boiling approximately 30 minutes.
 - 11.4.6 Once the samples reach near boiling, turn the heat down to medium.
 - 11.4.7 Add enough concentrated NH₄OH with a squirt bottle to reach the bromocresol purple indicator end point and form Ca₃(PO₄)₂ precipitate.
 - 11.4.8 Allow the sample to heat for another 20-30 minutes.
 - 11.4.9 Remove from the hot plate, allow sample to cool and precipitate to settle.
 - 11.4.10 Decant.
 - 11.4.11 Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 5 minutes at 2000 rpm.
 - 11.4.12 Decant supernatant and discard to waste.
 - 11.4.13 Proceed to section 11.5

- 11.5 Thorium/Plutonium/Uranium Separation using Eichrom resins.
- 11.5.1 Dissolve calcium phosphate precipitate, soil dissolution residue or evaporated water sample with 15 mL of Load solution. Vortex the sample.
- 11.5.1.1 **For waters:**
- 11.5.1.1.1 A additional 5 mL load solution aliquots may be necessary to dissolve the sample residue. Do not use more than 30 mL of load solution.
- NOTE: Samples that are high in carbonates and phosphates, as indicated by a violent and /or vigorous reaction during the initial phases of digestion, need to be loaded in a minimum of 40 mL of load solution.**
- 11.5.1.1.2 If particles are observed or the solution is cloudy, centrifuge the sample at approximately 2000 rpm for 5 minutes.
- NOTE: The use of filtration is also permitted, e.g. syringe filter if the solution is still cloudy.**
- 11.5.2 For each sample dissolved in load solution, place a UTEVA resin cartridge in the vacuum box. Lock a TEVA Resin cartridge onto the top of the UTEVA cartridge. Attach a plastic syringe funnel to the top of the TEVA cartridge.
- 11.5.2.1 **If samples do not require Uranium analysis, the UTEVA cartridge is omitted.**
- 11.5.3 Place a waste collection reservoir inside the vacuum box to catch the column effluent.
- 11.5.4 Just prior to loading the sample condition the resin:
- 11.5.4.1 Turn on the vacuum pump.
- 11.5.4.2 Add 5 mL of 3M HNO₃ into each funnel.
- 11.5.4.3 Allow the solution to be pulled through the columns by adjusting the flow rate on top of the vacuum box.
- 11.5.4.4 The flow rate should be approximately 3 mL per minute. Discard effluent to waste.
- NOTE: Approximately 20 drops equals 1 mL. Use the valve to adjust the flow for each individual sample. Adjust the flow for each solution added.**
- 11.5.5 For samples requiring Plutonium analysis (If samples do not require Plutonium, proceed to step 11.5.8):
- 11.5.5.1 Add 1 drop of Ammonium Thiocyanate and 1 mL of ascorbic acid solution to the sample load solution in the centrifuge tube and heat in hot water bath for approximately 5 minutes.
- 11.5.5.1.1 After heating, if samples are still red in color (indication of iron present in sample), add ascorbic acid drop wise until red color disappears. Heat in hot bath for 3 minutes.
- 11.5.5.2 Add 1 mL of NaNO₂ solution to the sample load solution in the centrifuge tube and heat in hot water bath for approximately 5 minutes.
- 11.5.5.3 Remove samples from hot water bath and let cool in cold water bath until samples are at or slightly below room temperature.
- 11.5.6 Transfer each sample load solution into the appropriate TEVA/UTEVA Resin cartridge funnel. Allow to drain. Adjust the flow rate to approximately 1 mL per minute.
- NOTE: the TEVA and the UTEVA cartridge can turn blueish green as the load solution drains through it.**
- 11.5.7 Rinse the funnel with 20 mL of 3M HNO₃ and allow to drain. Adjust flow to approximately 3 mL per minute.
- 11.5.8 Separate TEVA cartridge from UTEVA cartridge. Place new syringe on the UTEVA cartridge.
- NOTE: If Uranium analysis is not requested, the UTEVA cartridge is omitted.**

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11.5.9 Thorium Elution

11.5.9.1 Place a new clean labeled centrifuge tube in the rack beneath the TEVA cartridge.

11.5.9.2 Add 20 mL of 9M HCl into each cartridge and collect eluant. Adjust flow to approximately 1 mL per minute.

11.5.9.3 Add 5 mL of 6M HCl into each funnel and collect in the same centrifuge tube as in the previous step. This 6M HCl rinse will strip any residual traces of Thorium from the cartridge. Adjust flow to approximately 1 mL per minute.

11.5.9.4 For Thorium analysis:

11.5.9.4.1 Transfer the Thorium HCl solution to a clean labeled beaker (save centrifuge tubes) and evaporate to near dryness.

11.5.9.4.2 Add 5-10 mL of 1M HCl to the beaker and let sit for a few minutes to cool.

11.5.9.4.3 Transfer sample back to original centrifuge tube.

11.5.9.4.4 **To coprecipitate the Thorium**, proceed to ST-RC-0100, "Actinide Coprecipitation."

11.5.10 Plutonium Elution (**Thorium Elution step must be completed before this step- even if Thorium is not requested**)

11.5.10.1 Place a clean, labeled 50 mL centrifuge tube below each TEVA cartridge.

11.5.10.2 **For samples not suspected of containing Neptunium:**

11.5.10.2.1 **Plutonium Elution:**

11.5.10.2.1.1 Mix the 1M HCl and TiCl_3 by adding 10 mL of the 1M HCl to the column and pipetting 0.25 mL of the TiCl_3 into the column.

11.5.10.2.1.2 Add another 10 mL of 1M HCl.

11.5.10.2.1.3 Adjust the column box so that the flow is approximately 1 mL per minute.

11.5.10.2.2 **Collect the plutonium eluant**, and proceed to ST-RC-0100, "Actinide Coprecipitation."

11.5.10.3 **For samples suspected of containing Neptunium:**

11.5.10.3.1 **Plutonium Elution:**

11.5.10.3.1.1 Mix the HCl and TiCl_3 by adding 10 mL of 9M HCl to the column and pipetting 0.4 mL of the TiCl_3 into the column.

11.5.10.3.1.2 Add another 10 mL of 9M HCl.

11.5.10.3.1.3 Adjust the column box so that the flow is approximately 1 mL per minute.

11.5.10.3.1.4 **Collect the plutonium eluant.**

11.5.10.3.1.5 **To co-precipitate the Plutonium** proceed to ST-RC-0100, "Actinide Coprecipitation."

11.5.11 Uranium Elution (if requested)

11.5.11.1 Place a waste 50 mL centrifuge tube below each UTEVA cartridge.

11.5.11.2 Add 5 mL of 3M HNO_3 into each cartridge, adjust flow to approximately 3 mL per minute. Dispose to waste.

11.5.11.3 Add 5 mL of 9M HCl into each UTEVA cartridge and allow to drain. Adjust the flow rate to 1mL per/minute.

11.5.11.4 Discard this rinse.

NOTE: This rinse converts the resin to the chloride system. Some Neptunium may be removed here.

11.5.12 Add 20 mL of 5M HCl- 0.05M oxalic acid into each cartridge. Adjust flow rate to 1 mL per/minute and allow to drain. Discard this rinse.

Note: This rinse removes neptunium and thorium from the cartridge. The 9M HCl and the oxalic acid remove any residual ferrous ion.

11.5.13 Ensure that clean, labeled tubes are placed in the tube rack under the appropriate cartridge.

11.5.14 Add 15 mL of 1M HCl into each cartridge to strip the **Uranium**. Adjust flow rate to 1mL per/minute and allow to drain.

11.5.15 **To co-precipitate the Uranium** proceed to ST-RC-0100, "Actinide Coprecipitation."

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Density: Sample weight divided by the volume of said sample weight.

12.1.1 $D=M/V$ D=Density, M=Mass and V=Volume

12.2 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis ST-QAM. Specific analysis calculations are given in the applicable analytical SOP.

13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 Data assessment does not pertain to this sample preparation procedure.

13.1 Samples requiring re-preparation are submitted to the preparation lab with a NCM detailing the issue. The NCM process is described in SOP: ST-QA-0036. Specific information is given in the applicable analysis SOP.

14.0 METHOD PERFORMANCE

14.1 Method performance data, Reporting Limits, and QC acceptance limits, are maintained in LIMS.

14.2 Demonstration of Capability

1.2.1. Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification

1.3.1. The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

1.3.2. The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

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- 16.2 Waste Streams Produced by the Method
- 16.2.1 The following waste streams are produced when this method is carried out.
- 16.2.1.1 Acidic sample waste generated. All acidic waste will be accumulated in the appropriate waste accumulation container, labeled as Drum Type "A" or "B".
- 16.2.1.2 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash. If the lab ware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the lab ware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

17.0 REFERENCES

- 17.1 Eichrom Technologies, Inc Analytical Procedure "ACW13 VBS Thorium, Plutonium and Uranium in Water (with Vacuum Box System)". January 2003
- 17.2 Eichrom Technologies, Inc Analytical Procedure "ACW01 Uranium and Thorium, in Water". April, 2001
- 17.3 TestAmerica Quality Assurance Manual (ST-QAM), current revision
- 17.4 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.
- 17.5 Associated SOPs (current revisions)
- 17.5.1 ST-PM-0002, Sample Receipt and Chain of Custody
- 17.5.2 ST-QA-0002, Standards and Reagent Preparation
- 17.5.3 ST-QA-0005, Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes
- 17.5.4 ST-QA-0036, Non-conformance Memorandum (NCM) Process
- 17.5.5 ST-RC-0004, Preparation of Soil, Filter, Biota and Oil & Grease Samples for Actinide Analyses.
- 17.5.6 ST-RC-0100, Actinide Coprecipitation
- 17.5.7 ST-RC-5006, Decontamination of Laboratory Glassware, Labware and Equipment
- 17.5.8 ST-RD-0210, Daily Operations of an Alpha Spectroscopy System (using AlphaVision Software)

18.0 CLARIFICATIONS AND MODIFICATIONS TO REFERENCED METHODS

- 18.1 Ascorbic acid is used in place of ferrous sulfate to do the Plutonium valance adjustment.
- 18.1.1 We use ascorbic acid which provides the oxidation without introducing any iron, which is a known interference.
- 18.2 A 20 mL rinse is done instead of a 5 ml to ensure that all Uranium is rinsed from the cartridge.
- 18.3 The rinse steps are eliminated in the Plutonium separation step due to the larger rinse prior to the separation of the cartridge.
- 18.4 Plutonium is eluted with 20 mL 1M HCL to 25 mL TiCl_3 which serves to oxidize the Plutonium and strip it from the column in place of 25 mL of 0.05M HNO_3 /0.05M HF /0.02M TiCl_3 .
- 18.5 Bromocresol purple indicator is used throughout, where as the Eichrom method switches from Bromocresol purple to phenolphthalien indicator in mid-process.

19.0 CHANGES TO PREVIOUS REVISION

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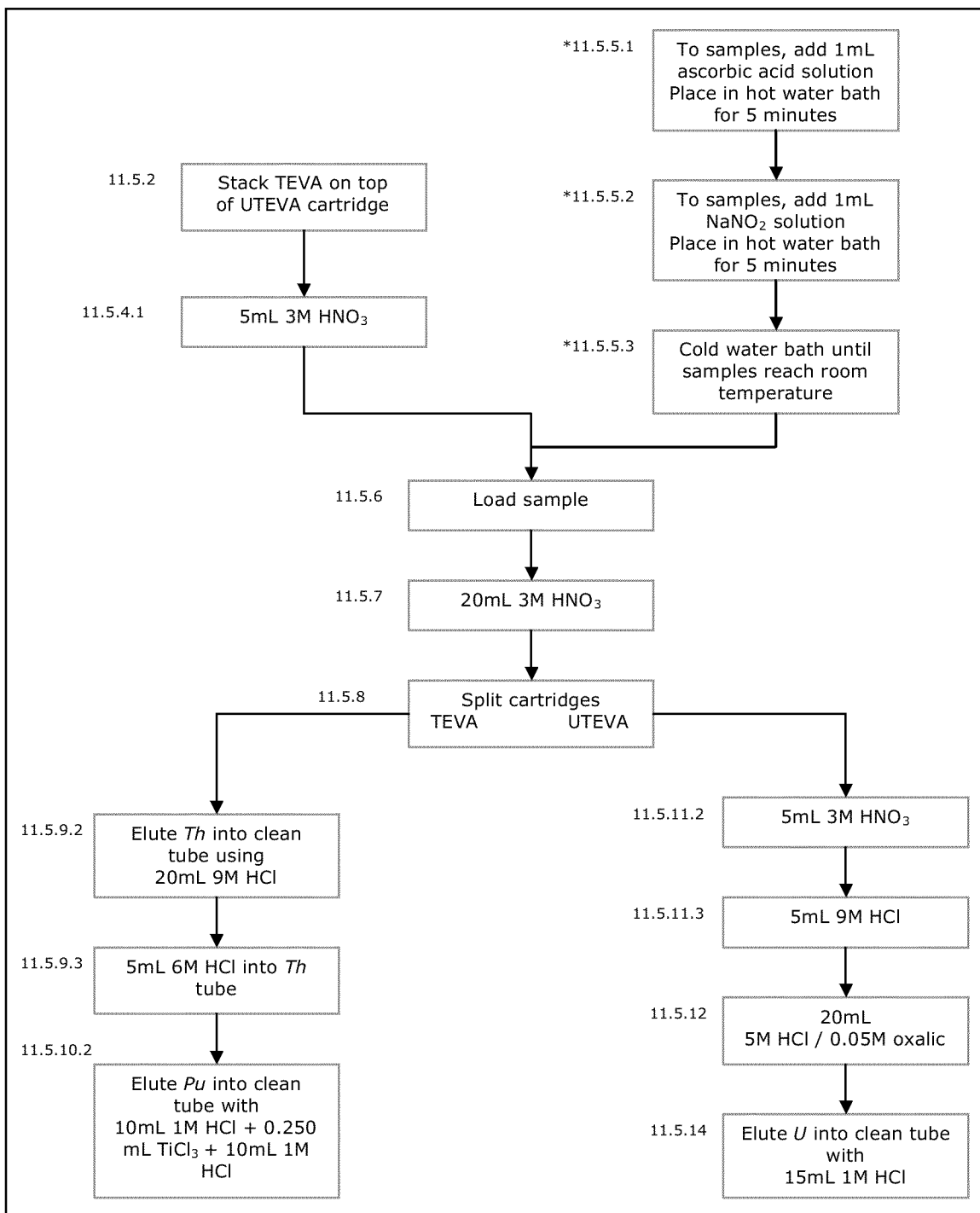
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- 19.1 Updated to TestAmerica format.
- 19.2 Updated standards and reagents in section 7.0 and removed Sulfuric Acid from list.
- 19.3 Updated procedure in section 11.0 regarding centrifuge time length and removed "Pipet" replacing it with "Add" throughout the section.
- 19.4 Rev. 13:
 - 19.4.1 Updated the section 11.4 in reference to the amount of time sample must remain in centrifuge.
- 19.5 Rev. 14:
 - 19.5.1 Added Hydrochloric Acid to Cresol Red indicator solution in section 7.9.
 - 19.5.2 Added a note to section 11.5.1.1.3 stipulating that samples with 5mL or more of gel/sediment need to go through a clean-up process.
 - 19.5.3 Added section 11.6 for Actinide Extraction from Gel/Sediment formation.
- 19.6 Rev. 15:
 - 19.6.1 Updated the summary of method in section 2.0.
 - 19.6.2 Updated equipment used in section 6.0.
 - 19.6.3 Updated reagents & standards throughout section 7.0.
 - 19.6.4 Removed the use of Cresol Red Indicator solution from section 7.0.
 - 19.6.5 Updated section 8.0 regarding storage, collection, pH testing and preservatives of samples.
 - 19.6.6 Added uranium to the list of analytes used for laboratory control samples in section 9.3.
 - 19.6.7 Updated section 11.0 regarding water sample prep, calcium phosphate precipitation and thorium/plutonium/uranium separation using Eichrom resins.
 - 19.6.8 Removed instruction for actinide extraction from gel/sediment formation in section 11.0.
 - 19.6.9 Updated calculation for sample density in section 12.0
- 19.7 Rev. 16:
 - 19.7.1 Section 7, removed reference to NIST traceable
 - 19.7.2 Section 8, removed holding time requirement
 - 19.7.3 Section 9, MB composition updated and LCS requirements updated.
 - 19.7.4 Section 11.5.5 updated
 - 19.7.5 Section 15 updated
- 19.8 Rev. 17:
 - 19.8.1 Grammatical Errors fixed through out SOP
 - 19.8.2 Updated Section 7.0 – updated Nitric acid make up in Section 7.13
 - 19.8.3 Updated Section 11.0 – added clarifications to procedure steps
 - 19.8.4 Updated Section 17.0 – update title of ST-RC-0004

Sequential Thorium, Plutonium and Uranium via TEVA/UTEVA

All rinses should flow at 1mL/minute (only 3M HNO₃ may be done at 3mL/minute)

*only necessary when analyzing for *Plutonium*



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